

Overview of Analysis Methods

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- Non-linear least square fitting of EXAFS data:
FEFF fitting and error analysis
- Linear least square fitting of EXAFS data:
Principal Component Analysis
- Tutorials and other materials:
<http://cars9.uchicago.edu/xafs/workshops.html>

FEFF Fitting and Error Analysis

Remove background: $\mu(E) \rightarrow \chi(k)$.

AUTOBK algorithm: M. Newville, P. Livins, Y. Yacoby, E. A. Stern, and J. J. Rehr, Phys. Rev. B47, 14126-14131 (1993).

Fourier transform data: $\chi(k) \rightarrow \tilde{\chi}(r)$

Pick a model

Calculate $f(k)$, $\delta(k)$ and $\lambda(k)$: FEFF

Fit theory to data

FEFF review: J.J. Rehr & R.C. Albers, Rev. Mod. Phys. (2000) 72, 621-654

Error analysis $\{x_i \pm \delta x_i\}$

Theoretical EXAFS Equation:

Single scattering path:

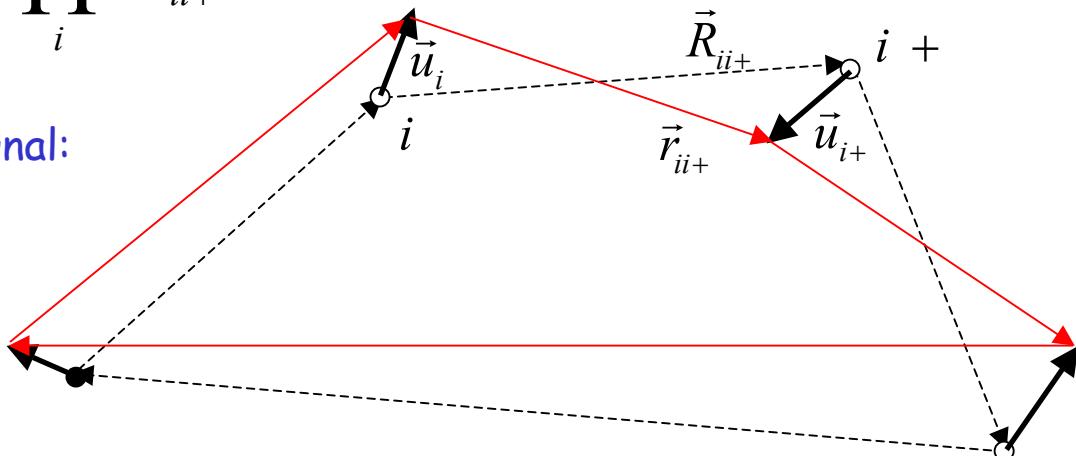
$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} |f^{\text{eff}}(k)| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin[2kR - \frac{4}{3}C_3 k^3 + \delta(k)]$$

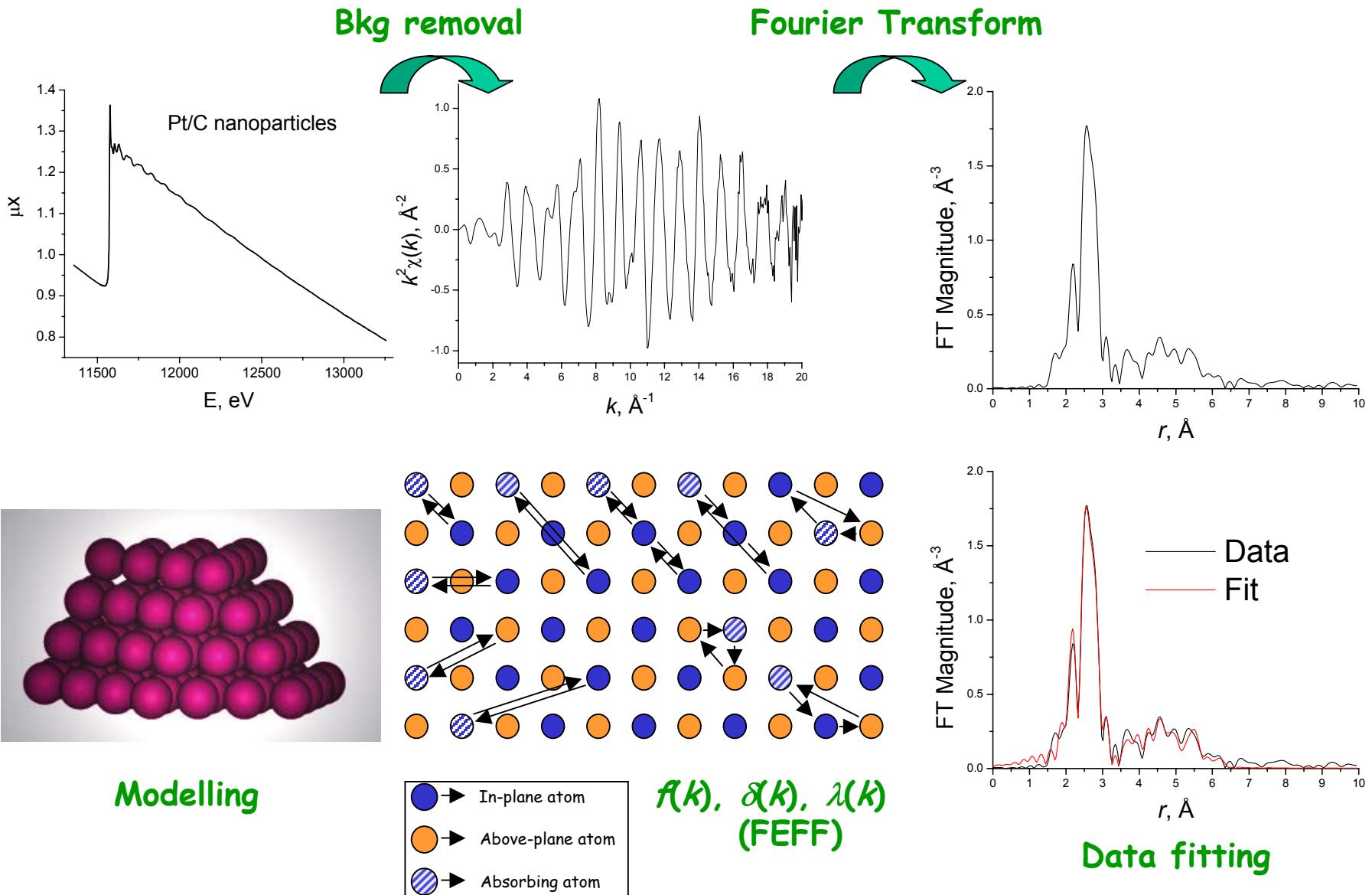
Multiple-scattering path:

$$\chi_{\Gamma}(k) = \text{Im } NS_0^2 \frac{e^{i \left(k \sum_i R_{ii+} + 2\delta(k) \right)}}{\prod_i kR_{ii+}} e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \text{Tr } MF^N \dots F^2 F^1$$

Theoretical EXAFS signal:

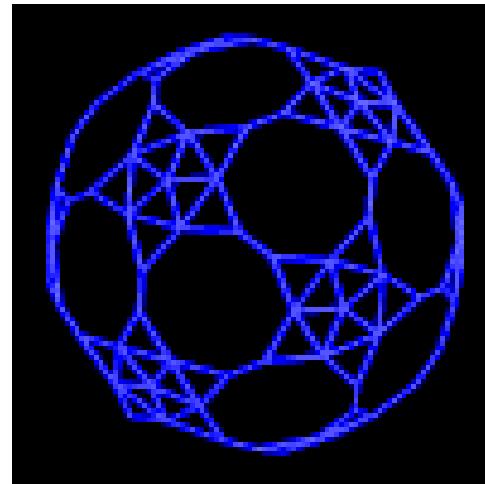
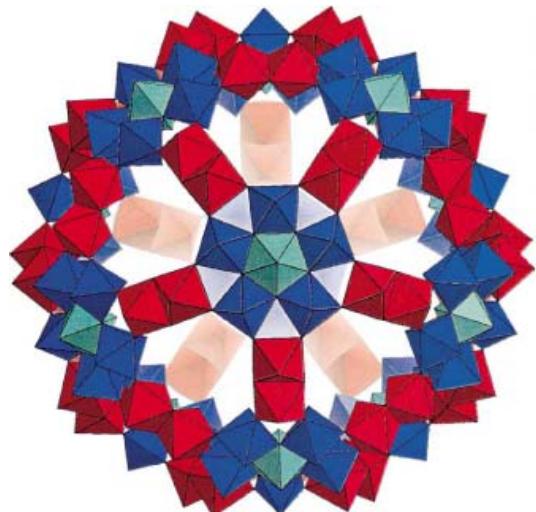
$$\chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k)$$



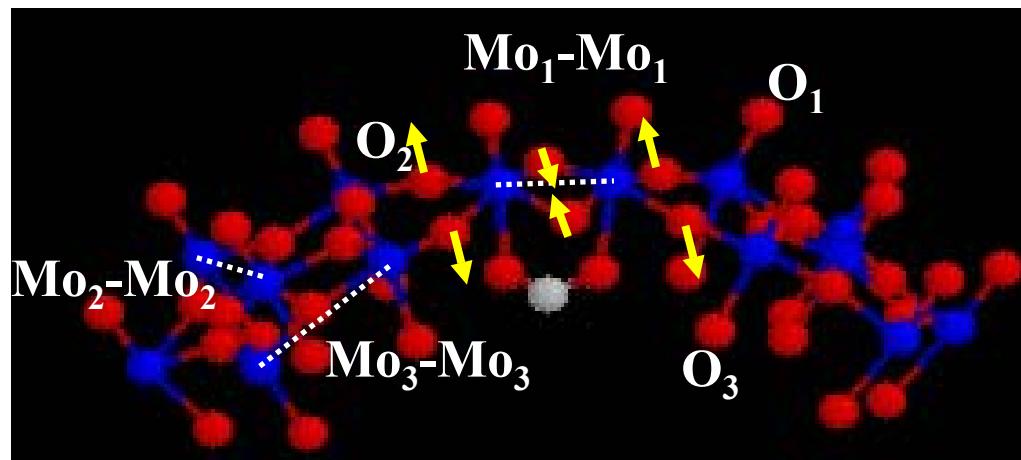


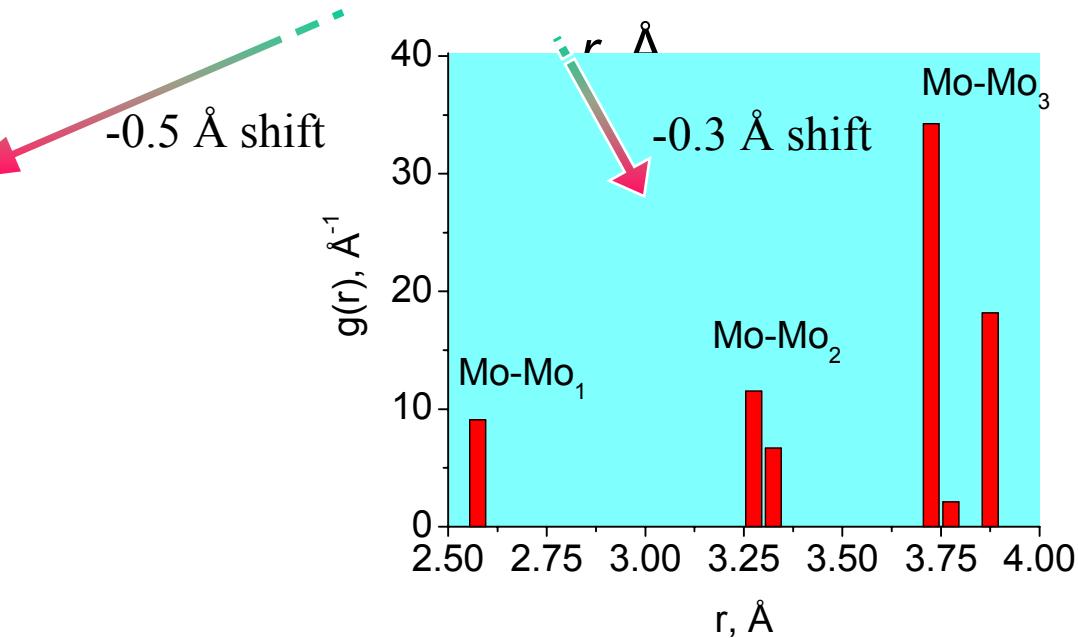
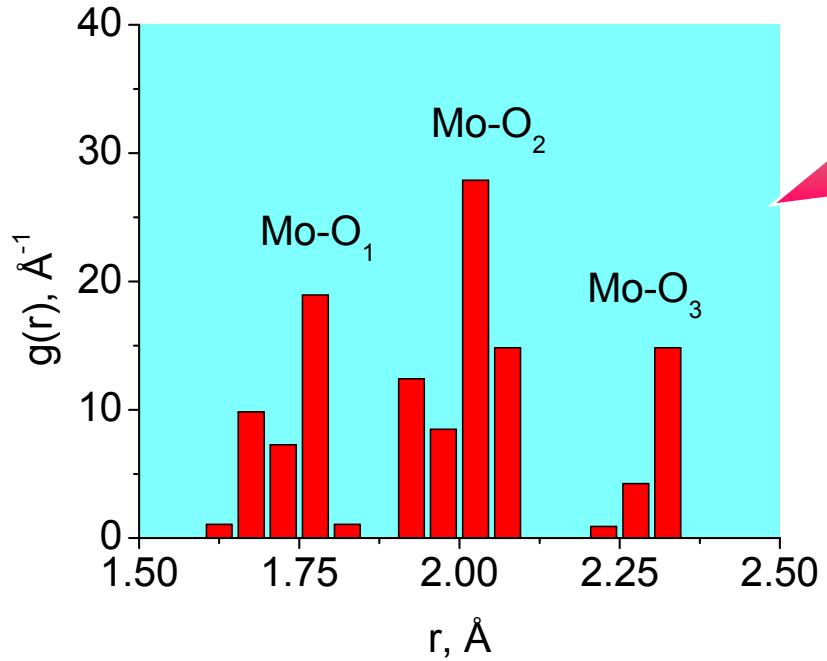
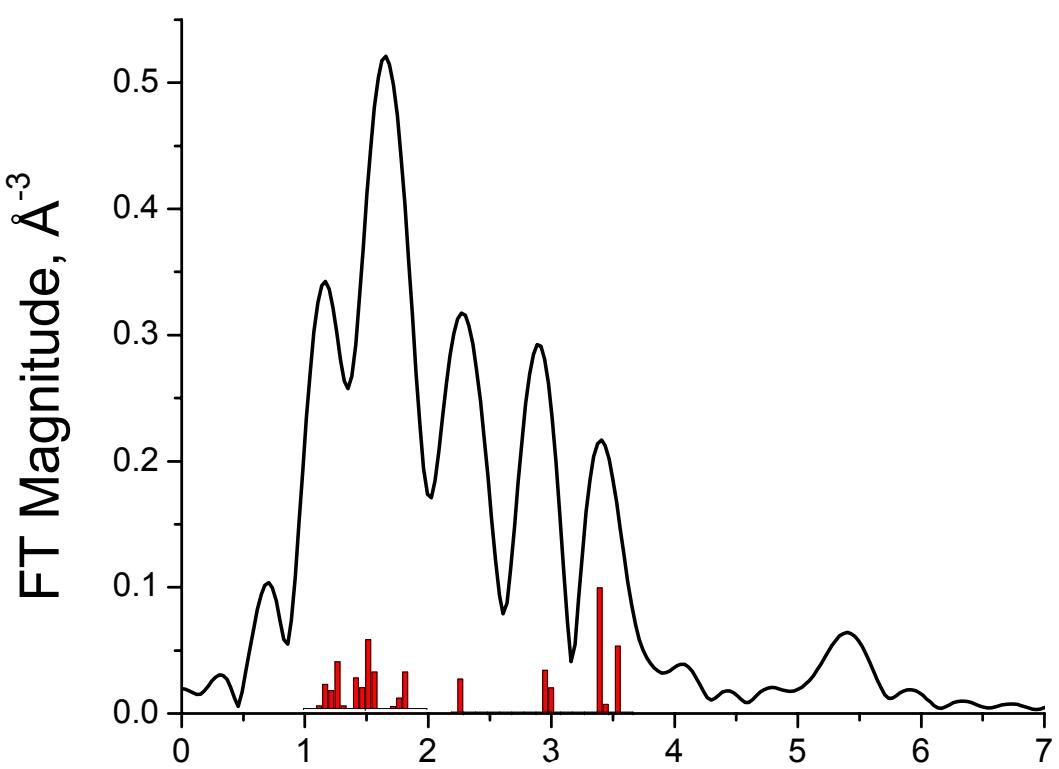
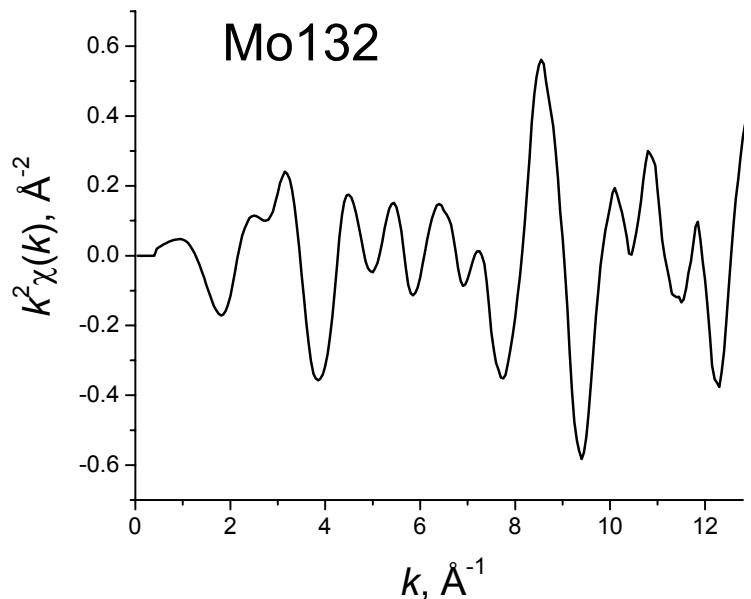
$\{\text{Mo}_{132}\}$ polyoxomolybdate

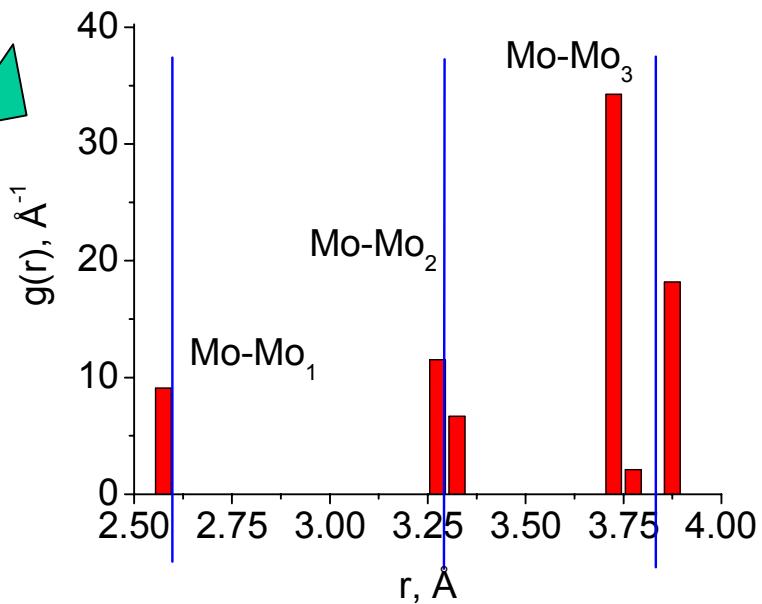
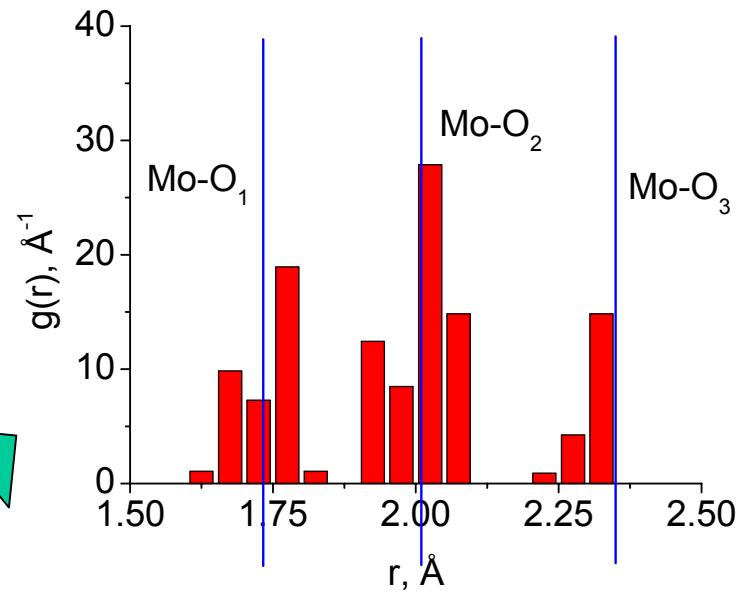
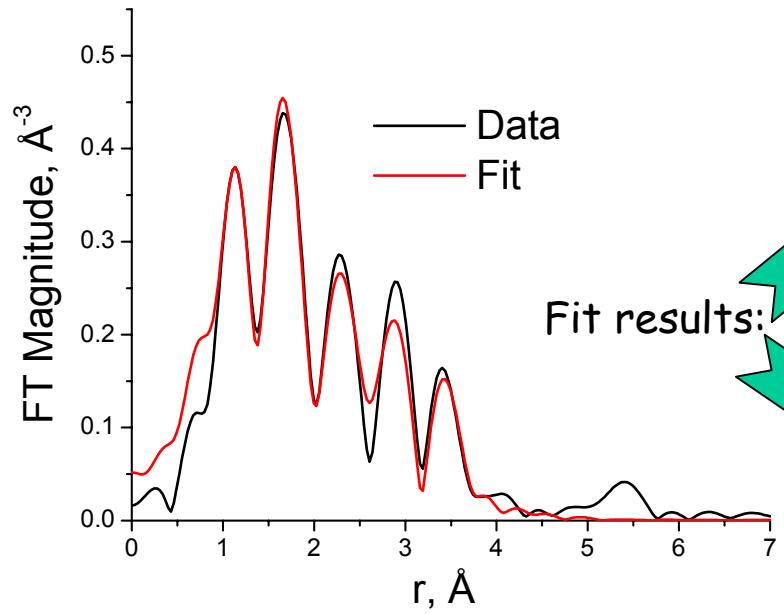
$[\text{Mo}_{132}\text{O}_{372}(\text{HCOO})_{30}]$



2.9 nm







Fourier Transforms in EXAFS:

$$\tilde{\chi}(R) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{i2kR} k^w \chi(k) \Omega(k)$$

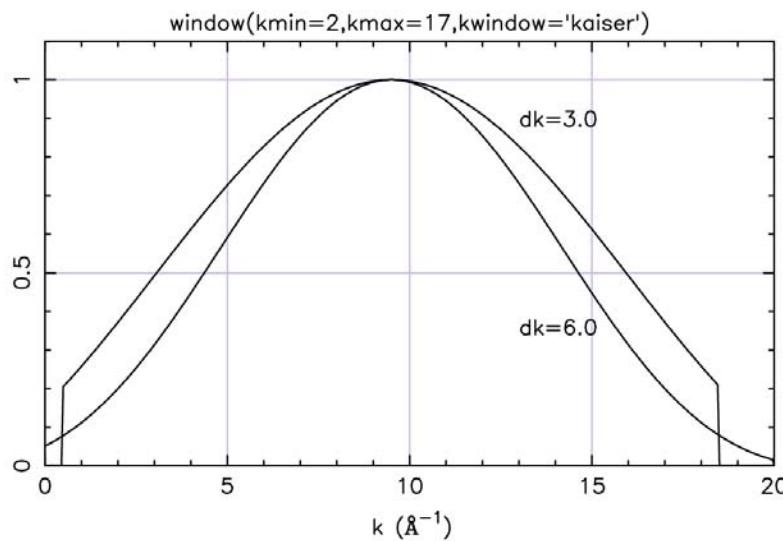
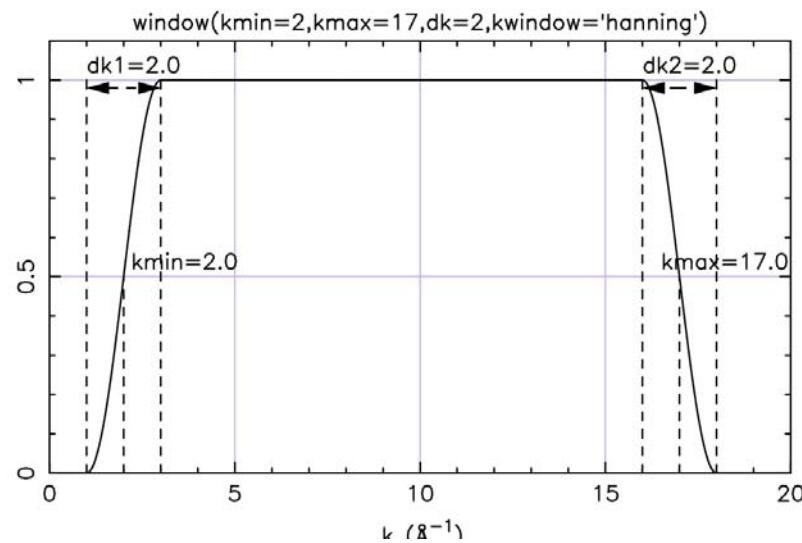
Example:

Matt Newville's IFEFFIT package uses FFT algorithms that implements discrete Fourier Transform:

$$\tilde{\chi}(R_m) = \frac{i\delta k}{\sqrt{\pi N_{\text{fft}}}} \sum_{n=1}^{N_{\text{fft}}} e^{i2\pi nm/N_{\text{fft}}} k_n^w \chi(k_n) \Omega(k_n)$$

Example: $\delta k = 0.05 \text{ \AA}$, $N_{\text{fft}} = 2048$ in IFEFFIT

Examples of Window Functions (M. Newville):



Fitting of EXAFS Theory to the Data:

$$f(R_i) = \tilde{\chi}(R_i) - \tilde{\chi}_{\text{M}}(R_i)$$

$$\chi^2_v = \frac{1}{v} \sum_{i=1}^{N_{\text{idp}}} \left(\frac{f_i}{\epsilon_i} \right)^2 = \frac{N_{\text{idp}}}{N v} \sum_{i=1}^N \left(\frac{f_i}{\epsilon_i} \right)^2$$

$$v = N_{\text{idp}} - P \quad (\text{Number of degrees of freedom})$$

$$N_{\text{idp}} = \frac{\Delta k \Delta R}{\pi} \quad (\text{Number of relevant independent data points})$$

E. A. Stern
Phys. Rev. B **48**, 9825-9827 (1993)

$$\chi^2_v = \frac{1}{v} \sum_{i=1}^{N_{\text{idp}}} \left(\frac{f_i}{\epsilon_i} \right)^2 = \frac{N_{\text{idp}}}{N v \epsilon} \sum_{i=1}^N \left[\text{Re}(f_i)^2 + \text{Im}(f_i)^2 \right]$$

Definition of Parameter Space:

In IFEFFIT, parametrization is the same for SS and MS paths:

$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} |f^{\text{eff}}(k)| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin \left[2kR - \frac{4}{3} C_3 k^3 + \delta(k) \right]$$

FEFF

Amplitude

$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)}$

$E_0 = E_0^{\text{bkg}} + \Delta E_0$

$R = R_{\text{model}} + \Delta R$

$$\chi_M(k) = \sum_{\Gamma} \chi_{\Gamma}(k) = \chi_M(x, k)$$

$x \in \Re^P$: vector in parameter space

$\chi_{\nu}^2(x) : \Re^P \rightarrow \Re$ Goodness of fit (cost function):

Taylor expansion near minimum: $\chi_{\nu}^2(x + h) \approx \chi_{\nu}^2(x) + h^T g + \frac{1}{2} h^T \mathbf{H} h$

$$g = \nabla_i \chi_{\nu}^2(x) = \begin{bmatrix} \frac{\partial \chi_{\nu}^2}{\partial x_1} \\ \vdots \\ \frac{\partial \chi_{\nu}^2}{\partial x_P} \end{bmatrix}$$

$$\mathbf{H} = \begin{bmatrix} \cdots & \cdots & \cdots \\ \cdots & \frac{\partial^2 \chi_{\nu}^2}{\partial x_i \partial x_j}(x) & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} \quad (\text{Hessian matrix})$$

How does the **Levenberg-Marquardt** algorithm work:

The **Steepest Descent Method** (if the initial guess is far from the minimum):

Descending condition: $x[k] = x[k-1] + h_d$

$$\chi^2_v(x[k]) < \chi^2_v(x[k-1])$$

The Steepest Descent condition: $h_d = h_{sd} = -g = -\nabla_i \chi^2_v(x)$

However, conversion is slow near the minimum. There, LM algorithm uses the **Newton-Gauss Method**:

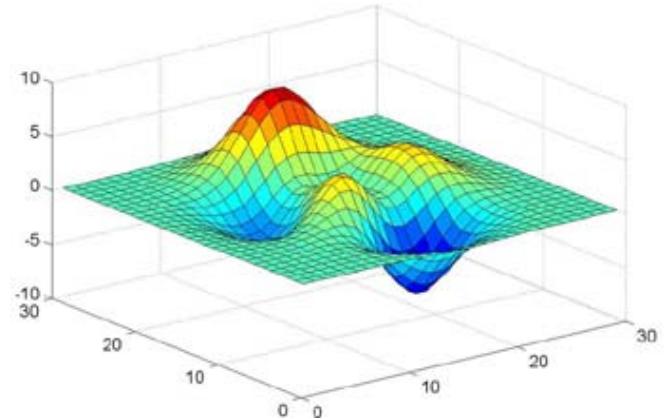
$$g(x+h) \approx g(x) + \mathbf{H}h$$

- Iterative process:
- 1) Find $h_a : \mathbf{H}h_a = -g(x[k-1])$
 - 2) $x[k] = x[k-1] + h_a$

To find uncertainty δx_i in the best fit result for x_i : $\delta x_i = \sqrt{(H_{ii})^{-1}}$

Physical meaning:

since $H = \begin{bmatrix} \dots & \dots & \dots \\ \dots & \frac{\partial^2 \chi^2}{\partial x_i \partial x_j}(x) & \dots \\ \dots & \dots & \dots \end{bmatrix}$



The second derivative: rate of curvature of the curve.

The higher second derivative,
the higher rate of curvature,
the more this variable affects the fit.

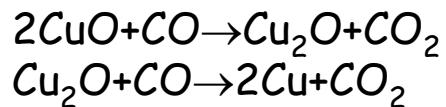
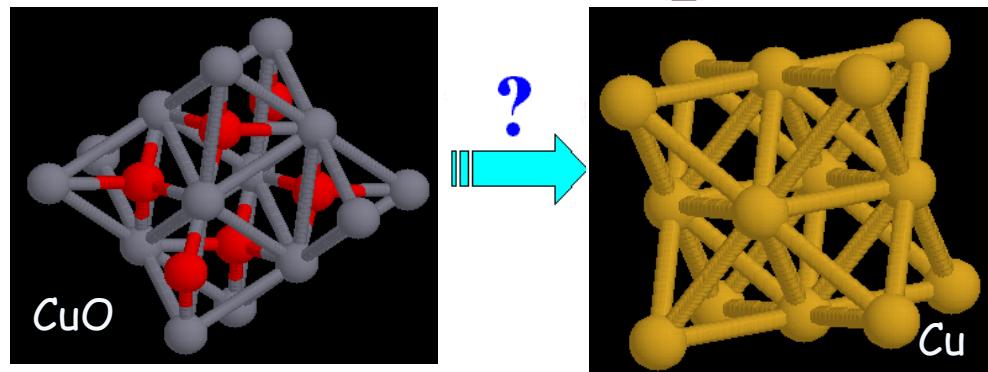
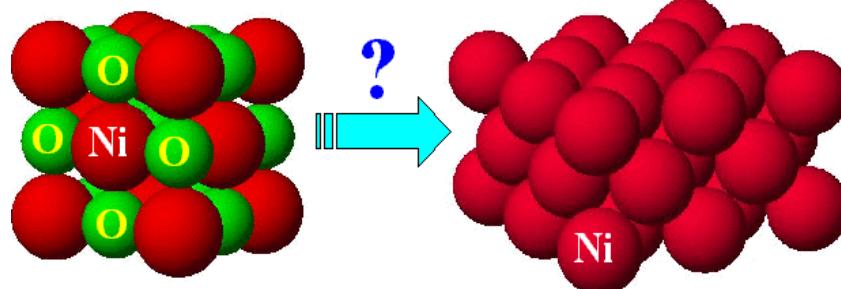
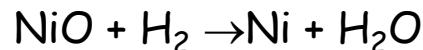
When we invert the second derivative for such a variable,
the standard deviation becomes small and vice versa.

Principal Components Analysis of EXAFS Data

A. I. Frenkel, O. Kleinfeld, S. Wasserman and I. Sagi,
J. Chem. Phys., 116, 9449 (2002).

J. Rodriguez, J. Hanson, A.I. Frenkel, et al:
JACS 124, 346 (2002),
JACS 125, 10684 (2003),
JPCB 108, 13667 (2004)

- Oxidation/Reduction of Metal Oxides;
- Electrochemical Oxidation/Reduction;
- Nucleation and Growth of Nanophase;
- etc.



What structural transformations occur on the atomic scale?
Questions: Any short-living, strongly distorted intermediate phases?
What is the reaction kinetics at different temperatures?

N data sets, M energy points in each measurement \Rightarrow data matrix $A(N,M)$

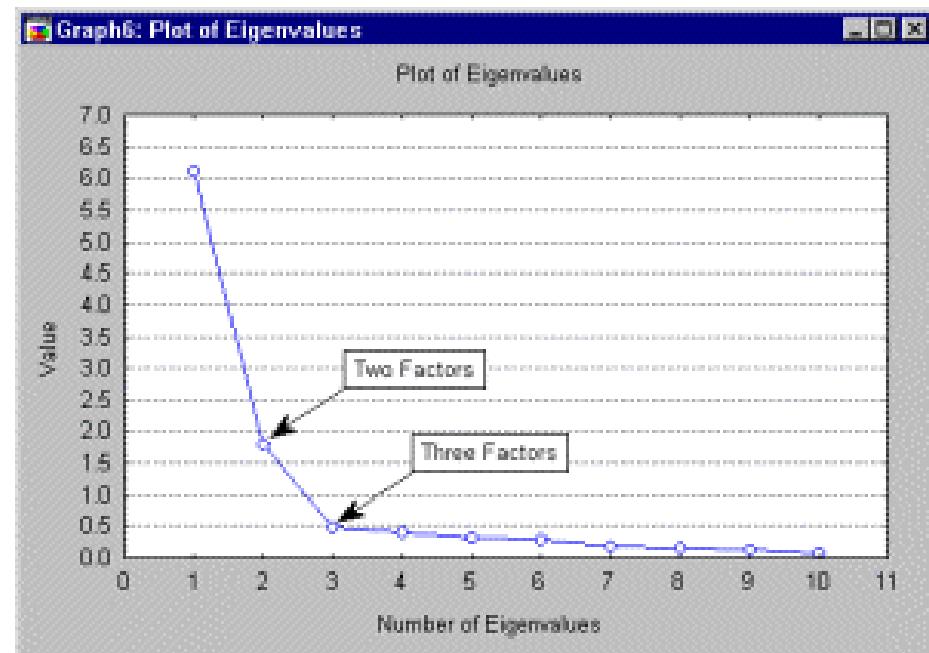
Data	Eigenvectors (components)	Eigenvalues (importance of the components)	Eigenvectors (importance of the components for individual spectrum)
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$$\begin{pmatrix} A \\ M \times N \end{pmatrix} = \begin{pmatrix} U \\ M \times N \end{pmatrix} \cdot \begin{pmatrix} \lambda_1 & \lambda_2 & \dots & \lambda_N \\ N \times N \end{pmatrix} \cdot \begin{pmatrix} V^T \\ N \times N \end{pmatrix}$$

$$\lambda_1 > \lambda_2 > \dots > \lambda_N$$

How to determine the number of dominant components sufficient to represent the data?

The **scree test**





2-D (46x46)
array of
intensity values

Adapted from Qing Jiang,
University of Chicago

The set F of $m = 593$ face images was formed by the 2-D (46x46) arrays of intensity values, or vectors in $k = 2116$ space:

$$F = \{\mathbf{f}_i \in \mathbf{R}^k, i = 1, \dots, m\} \subset \mathbf{R}^k$$

But: $\{\mathbf{f}_i\}$ are not randomly distributed in the \mathbf{R}^k space:
all faces have the same facial features (eyes, nose, mouth etc.)
 \Rightarrow all the faces form a subset of the whole image space:

$$F \subset \mathbf{R}^n \subset \mathbf{R}^k \quad (n \ll k)$$

i.e., the dimension of the face space (n) is much smaller than that of the image space (k).

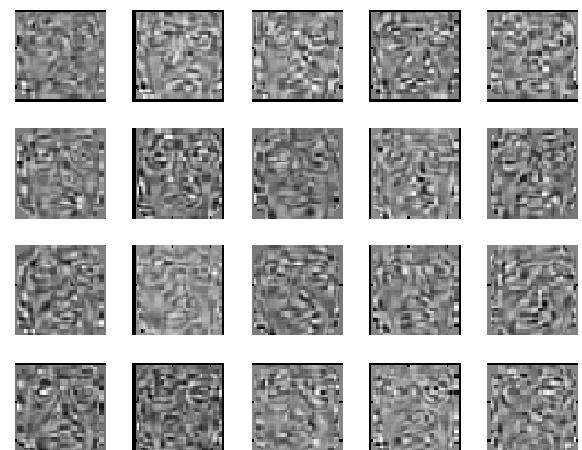
PCA creates a new n -dimensional coordinate system, with the basis \mathbf{X} :

$$\mathbf{X} = \{\mathbf{x}_i \in \mathbf{R}^k, i = 1, \dots, n\}$$

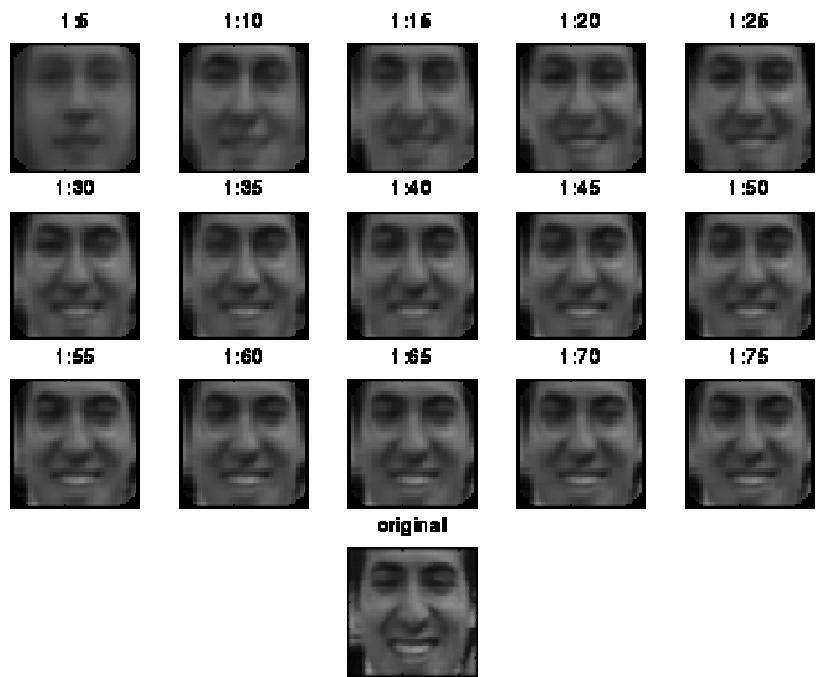
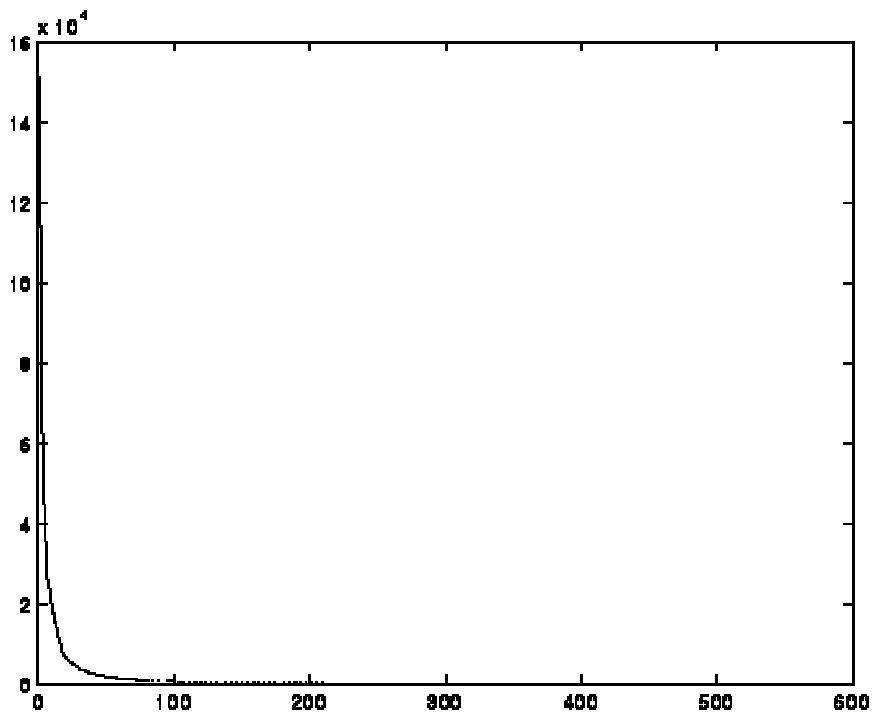
where coordinates \mathbf{x}_i are part of the eigenvectors (**eigenfaces**) of a set of face images.
Each face can be reconstructed with only part of its projections (principal components)
onto the new low-dimensional space \mathbf{X} .



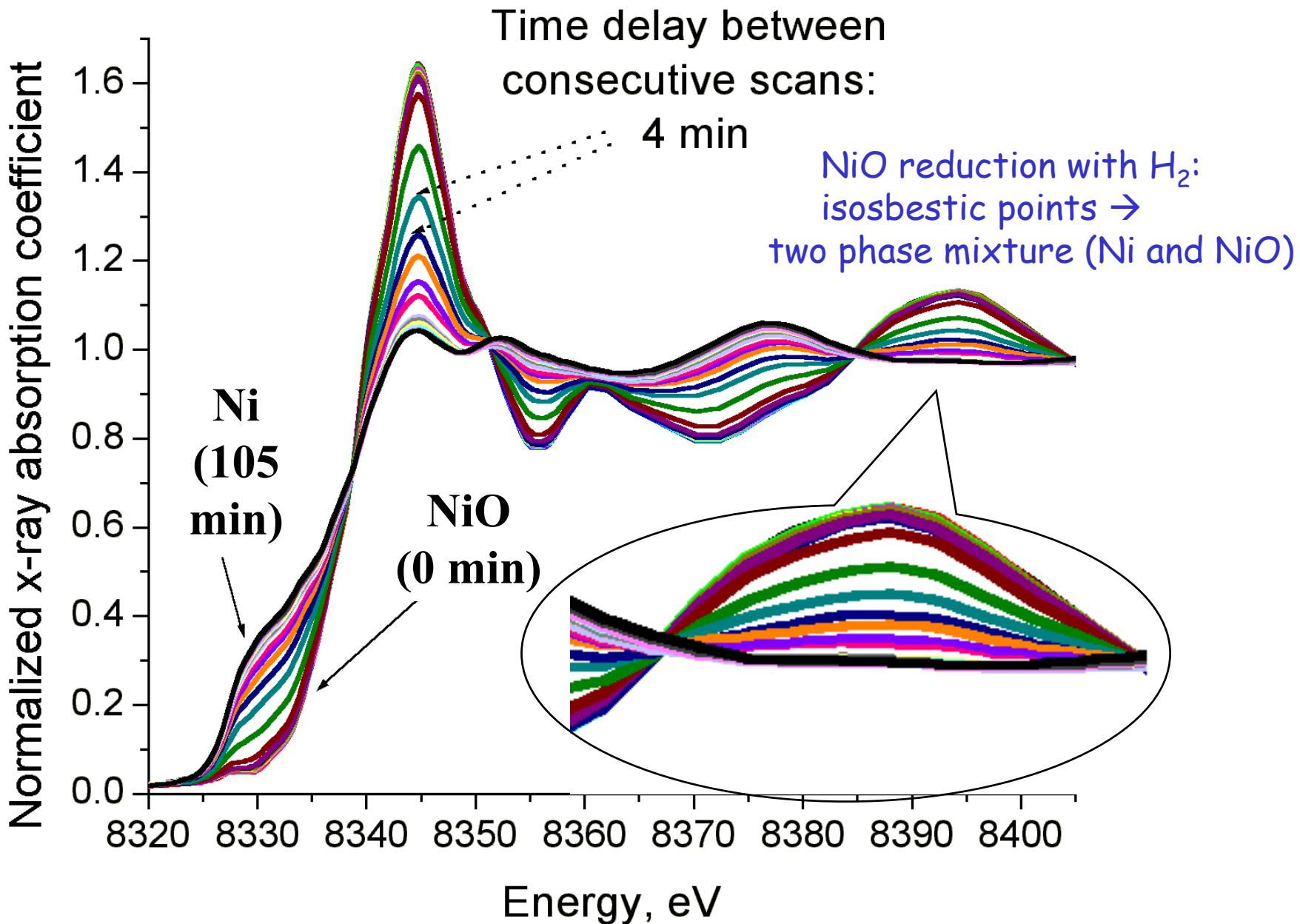
The first 20
eigenfaces with the
highest eigenvalues

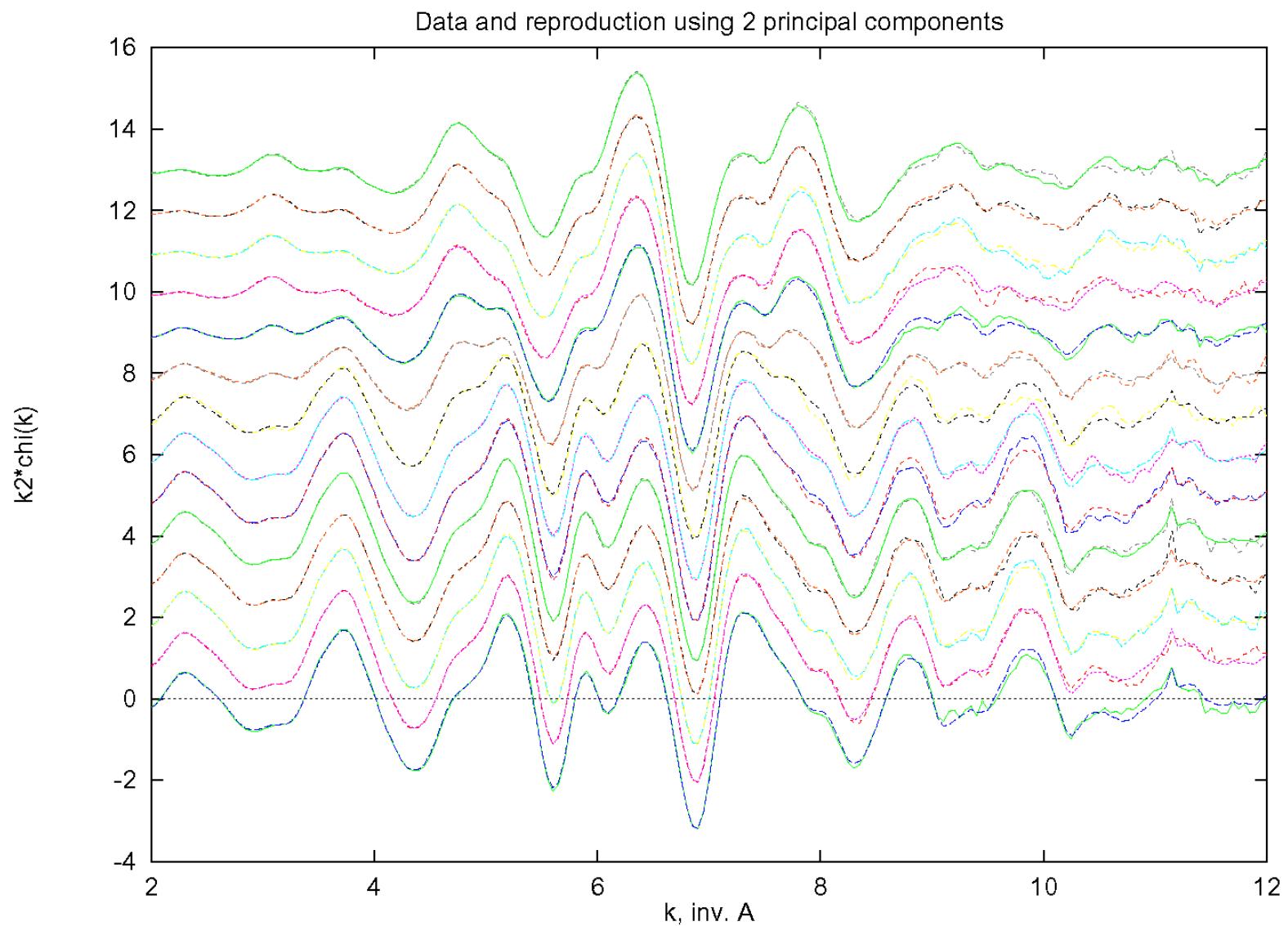


Eigenfaces with
eigenvalues ranked from
141 to 160



Faces reconstructed using eigenfaces with high eigenvalues. The label above each face is the range of eigenfaces used

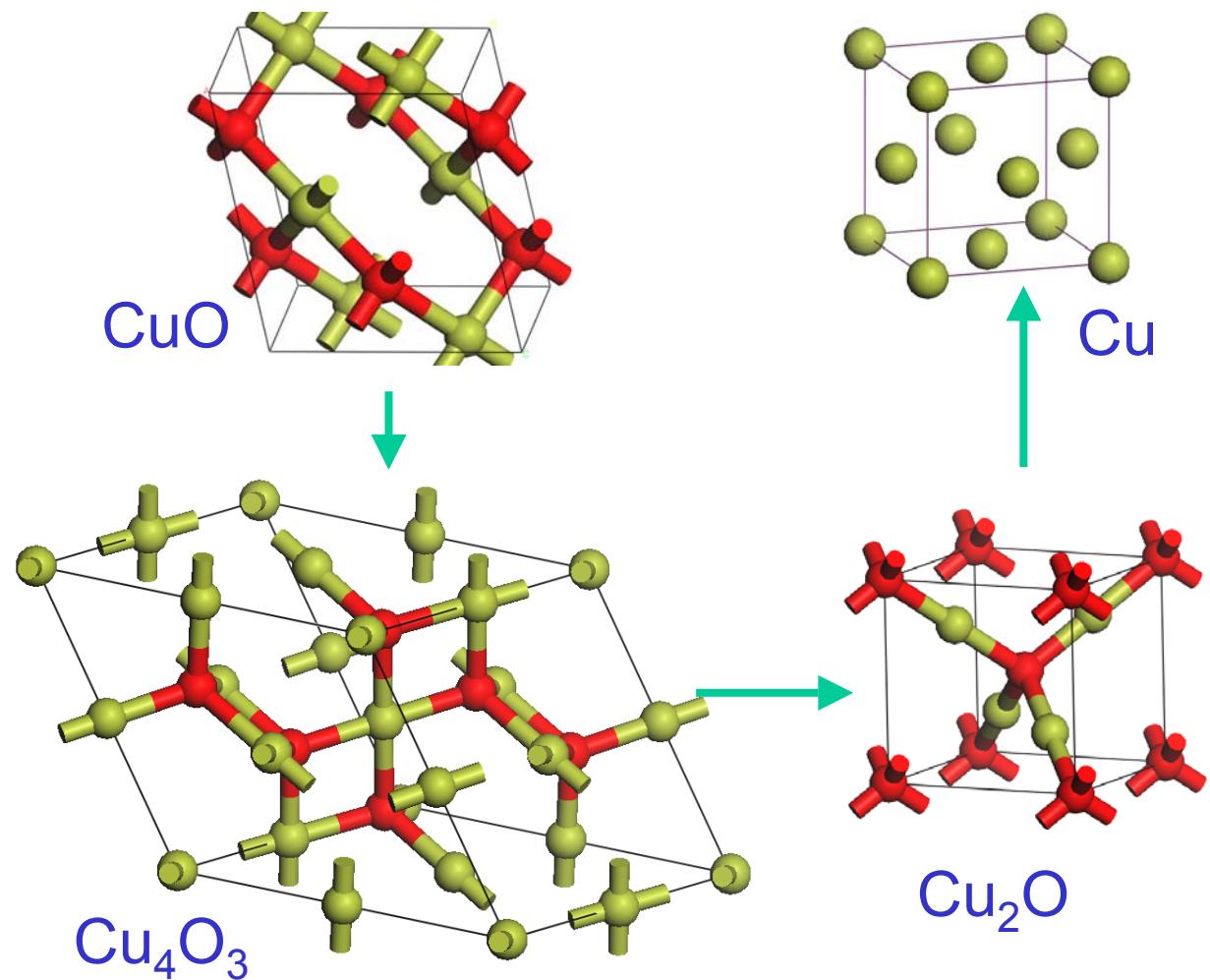
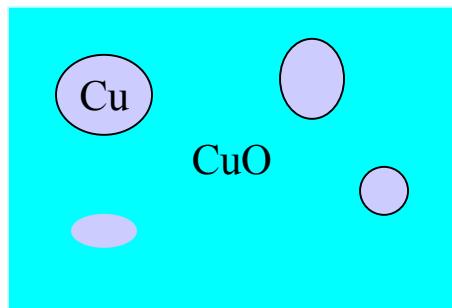


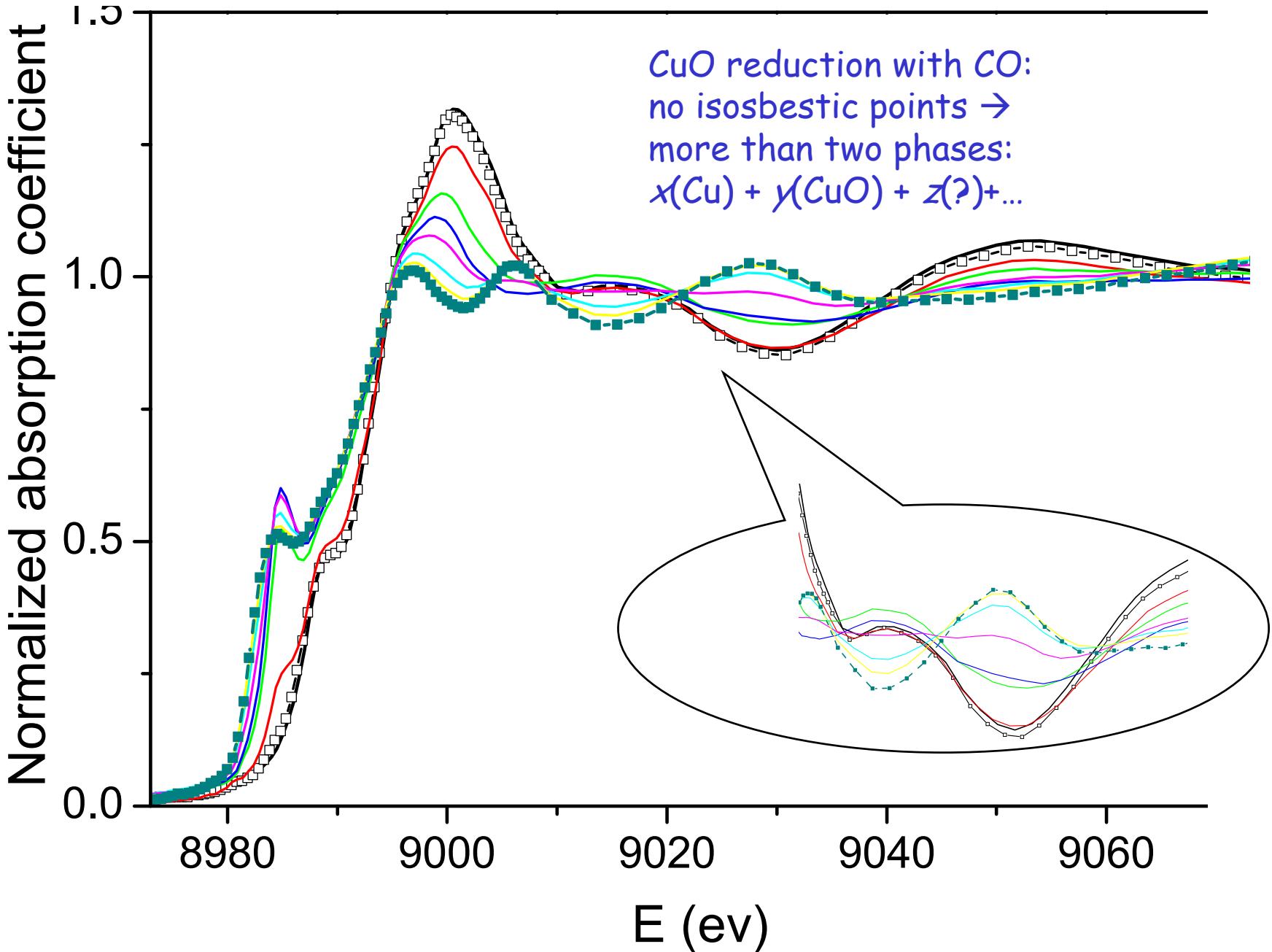


Two alternative models:

2) Sequential reduction

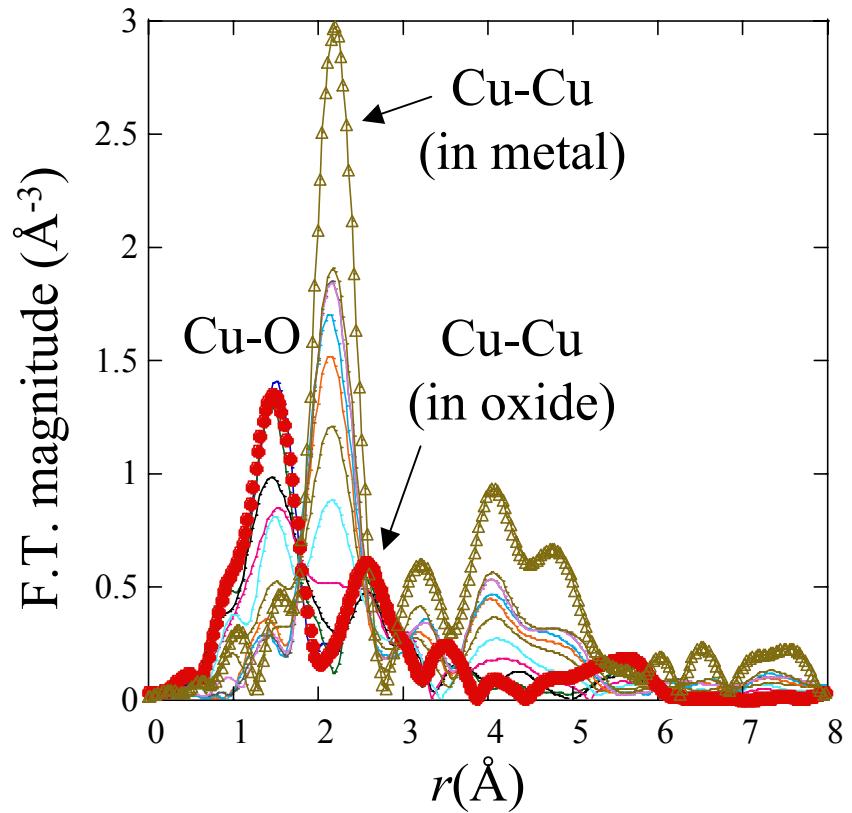
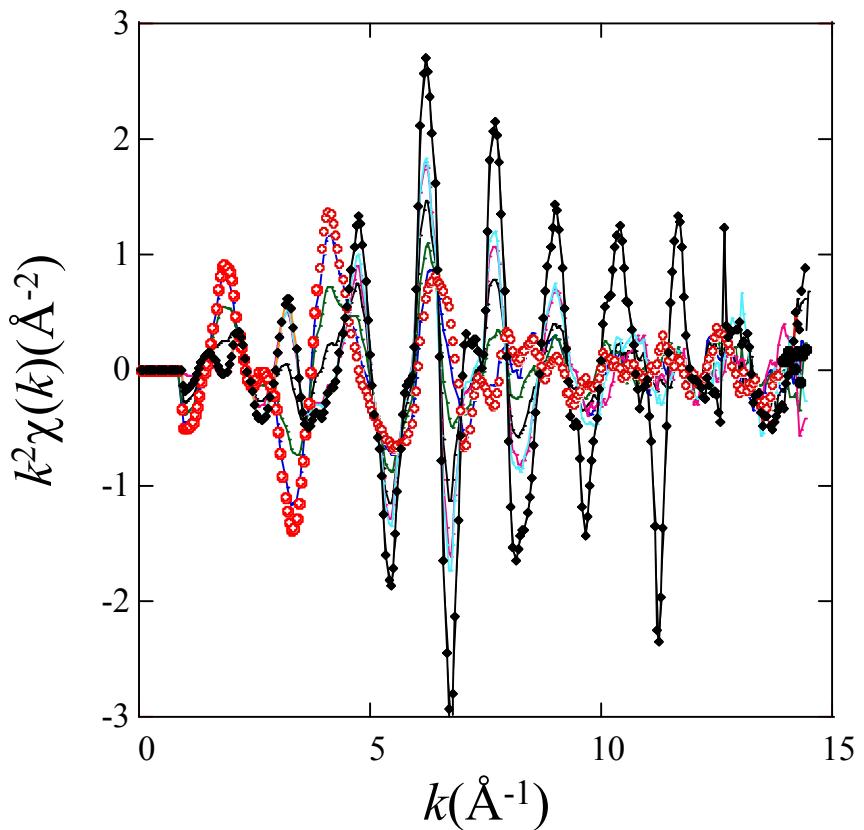
1) Non-uniform reduction



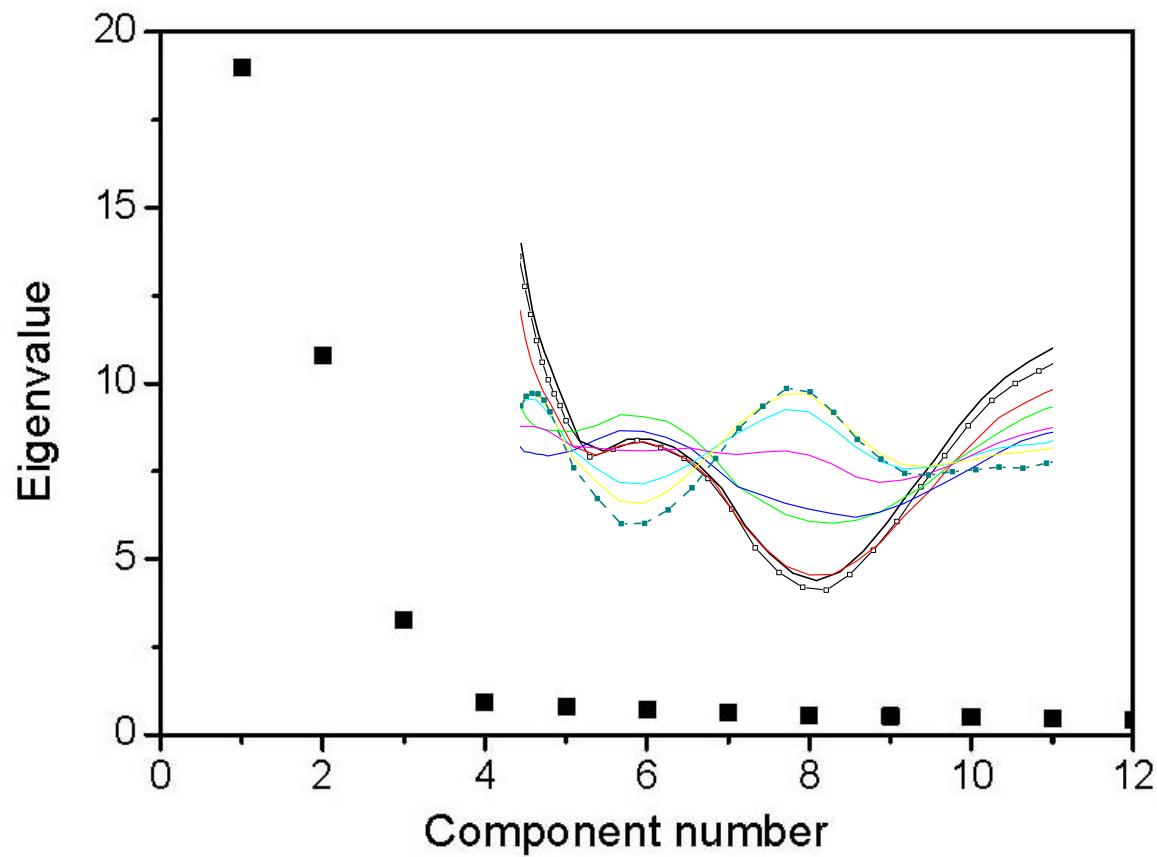


From Face Recognition: to Phase Recognition

Time-Resolved EXAFS



Scree test in CuO (reduced with CO)



Principal Component Analysis of TR EXAFS

CuO reduction with CO: three phase mixture

